Unit 4

Answers: First Law of Thermodynamics

Quick checks

1 b Nothing gets in or out of the sealed bottle, so no matter crosses its boundary; but heat flows in from the warm air through the glass, and the drink warms up. Energy crosses, matter doesn't: a **closed** system. Being sealed is not enough to be isolated; it would also need to be insulated.

2 c Heat is energy **in transfer**, and how much is given depends on the path taken between two states, so it is a process variable, like work. Temperature, volume and internal energy each have one definite value in a given equilibrium state.

3 b Anticlockwise, the gas expands along the lower curve (at low pressure, little work done by it) and is compressed along the upper curve (at high pressure, more work done on it). The net work done by the gas is negative, the loop's area. The gas returning to its first state makes $\Delta U = 0$, not $W = 0$.

4 b $\Delta U = Q - W = 500 - 200 = 300$ J, a rise. 700 J would come from adding the work instead of subtracting it: the work done by the gas carries energy **out**.

5 b A diatomic molecule has 3 translational and 2 rotational degrees of freedom (its vibrations are frozen at room temperature), so $f = 5$ and $\gamma = 1 + 2/5 = 1.40$. 1.67 is for a monatomic gas ($f = 3$) and 1.33 for a non-linear polyatomic one ($f = 6$).

6 c No heat flows, but work is done **on** the gas, and with nowhere to go, that energy raises its internal energy: $dU = -dW > 0$. So its temperature rises, by $T_2 = T_1 \times 2^{\gamma - 1}$, about 32% for air. "No heat" doesn't mean "no change in temperature": that confusion is the commonest slip in this unit.

7 c Slow, with no friction and no heat flowing across a temperature difference: every step can be reversed by a tiny change. Braking turns motion into heat by friction; ice in warm water takes in heat across a large temperature difference; a burst balloon's gas expands violently, out of equilibrium. All three are irreversible.

8 d Systems are classed by what crosses their boundary: matter and energy (open), energy only (closed) or neither (isolated). "Static system" is not one of these types.

9 c $dQ = dU + dW$ says heat given to a system all goes into its internal energy and the work it does: energy is conserved. Entropy is not conserved; it grows in every irreversible process (Unit 5).

10 c Adiabatic means $dQ = 0$, so $dU = -dW$: the work done by the gas equals the fall in its internal energy, and it cools.

11 **b** *Isothermal* means at constant temperature. The pressure and volume change ($PV =$ constant), and since heat flows in or out, so does the entropy. For an ideal gas the internal energy, which depends on T only, also stays constant.

12 **c** Mayer's relation: at constant pressure the gas also does work $P\,dV = R\,dT$ per mole, so C_P exceeds C_V by R. It is their **ratio** that is γ.

13 **c** $W = \int P\,dV$ and $dV = 0$, so no work is done: on the P–V diagram it is a vertical line with no area under it.

14 **a** $V_f/V_i = 3 > 1$, so $\ln 3 = 1.10 > 0$ and $W > 0$: an expanding gas does positive work.

15 **a** Work is done on the gas and no heat leaves, so its internal energy, and its temperature, rise: $TV^{\gamma-1} =$ constant, and V falls.

16 **b** Against a **constant** external pressure the work is simply that pressure × the change in volume:
$W = P\,\Delta V = 2 \times 1.013 \times 10^5 \times (4 - 1) \times 10^{-3} =$ **608 J**.
The formula $nRT\ln(V_2/V_1)$ is for a slow, reversible isothermal expansion, where the outside pressure is lowered step by step to match the gas's; it would give 3458 J only for 1 mole, which these numbers don't describe.

17 **a** $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$:
$T_2 = T_1\left(\dfrac{V_1}{V_2}\right)^{\gamma-1} = 300 \times 5^{0.4} = 300 \times 1.904 =$ **571 K**.
The number of moles doesn't matter. 1500 K would be 300×5, as if TV were constant.

18 **c** $P_2 = P_1\left(\dfrac{V_1}{V_2}\right)^{1.4} = 2 \times \left(\dfrac{3}{6}\right)^{1.4} = 2 \times 0.379 =$ **0.76 atm**. (At constant temperature it would have been 1 atm; the adiabatic fall is steeper.)

12. a. A **thermodynamic system** is a chosen part of matter or region of space, separated from its surroundings by a real or imagined boundary, whose energy changes we study.

	Open system	Closed system	Isolated system
Matter crosses the boundary	yes	no	no
Energy (heat, work) crosses	yes	yes	no
Example	water boiling in an open pot	gas in a conducting cylinder with a piston	hot tea in a stoppered vacuum flask

b. **Work done by the system** is done when it pushes its surroundings back (a gas expanding, $dV > 0$): the system gives energy to the surroundings, and the work is taken as positive. **Work done on the system** is done when the surroundings push it in (a gas compressed, $dV < 0$): the surroundings give it energy, and the work done by the system is negative. In both, $W = \int P\,dV$.

c. $W = P(V_2 - V_1) = 2 \times 10^5 \times (0.03 - 0.01) = 2 \times 10^5 \times 0.02 = \mathbf{4000\ J}$.

d. An **indicator diagram** is a graph of the pressure of a working gas against its volume during a process. The work done is the area under the curve: in a small step the volume grows by dV at pressure P, doing work $P\,dV$, the area of a thin strip under the curve (Figure 4.4); adding all the strips, $W = \int_{V_1}^{V_2} P\,dV =$ the area between the curve, the volume axis and the lines $V = V_1$ and $V = V_2$. For a cycle, the net work is the area of the loop.

13. a. The **internal energy** of a system is the total kinetic and potential energy of its molecules. It is a state function, and it changes in two ways: heat flowing in raises it, and work done by the system lowers it: $dU = dQ - dW$.
$dU = -dW$ is this for a process with no heat exchanged (adiabatic, $dQ = 0$): any work the system does comes out of its internal energy, so an expanding gas cools, and work done on it raises its internal energy, so a compressed gas heats up.
In an **ideal gas** the molecules don't attract, so there is no potential energy and U depends on the temperature only. In a **real gas** there is also potential energy from the attraction between molecules, which depends on their spacing, so U depends on both temperature and volume.
b. $\Delta U = nC_V\,\Delta T = 2 \times \frac{3}{2} \times 8.314 \times (500 - 300) = 3 \times 8.314 \times 200 = \mathbf{4988.4\ J}$ (about 4.99 kJ).

14.

a. **First law:** when heat dQ is given to a system, it is used to raise the system's internal energy (dU) and to do external work (dW): $dQ = dU + dW$, or for a gas, $dQ = dU + P\,dV$. Heat in, work out and stored energy always balance. **Significance:** it shows heat is a form of energy; it lets us find any one of heat, work and change of internal energy from the other two; it makes internal energy a state function; it rules out a machine that gives work without taking in energy; it is the basis of the study of engines, refrigerators, chemical reactions and living things.

b. Yes. It is the law of conservation of energy applied to processes involving heat: no energy is created or lost, only shared between internal energy and work.

c. $\Delta U = Q - W = 600 - 150 = \mathbf{450\ J}$ (an increase).

d. i. It doesn't tell the direction in which heat flows, or why it never flows by itself from cold to hot. ii. It doesn't give the conditions under which heat can be turned into work. iii. It doesn't say that, although work can be turned completely into heat, heat can't be turned completely into work in a cycle. iv. It doesn't say how much of the heat taken in can become work (the limit to an engine's efficiency).

15.

a. The heat needed to warm a gas depends on whether it is allowed to expand. If it expands, it does work, which needs extra heat; if not, it doesn't. Since a gas can be heated in many ways, it has many heat capacities; the two standard ones are at constant volume (C_V) and at constant pressure (C_P). A solid or liquid expands so little that the difference hardly matters.

b. For one mole of ideal gas:

1. At constant volume, no work is done, so $dQ_V = dU$, and $dU = C_V\,dT$. Since U depends only on T, this dU is the same for any process with the same dT.
2. At constant pressure: $dQ_P = dU + P\,dV$, so $C_P\,dT = C_V\,dT + P\,dV$.
3. From $PV = RT$ at constant P: $P\,dV = R\,dT$.
4. So $C_P\,dT = C_V\,dT + R\,dT$, and dividing by dT: $C_P - C_V = R$.

c. At constant pressure the gas expands as it warms and does work against its surroundings, so it needs the heat for the rise in internal energy **plus** the heat for this work (R per mole per kelvin). At constant volume no work is done. So $C_P = C_V + R > C_V$.

d. $R = C_P - C_V = 29.1 - 20.8 = \mathbf{8.3\ J/(mol\ K)}$; $\gamma = \dfrac{C_P}{C_V} = \dfrac{29.1}{20.8} = \mathbf{1.40}$ (a diatomic gas).

16. a. **Isothermal:** the temperature stays constant (slow change, conducting walls, in contact with a reservoir); $PV =$ constant, a hyperbola on the P–V diagram (Figure 4.9); $\Delta U = 0$, so the heat taken in equals the work done. **Adiabatic:** no heat is exchanged (insulated, or fast); $PV^{\gamma} =$ constant, a curve steeper than the isotherm (Figure 4.11); the work comes from the internal energy, so expansion cools the gas and compression heats it. **Isobaric:** the pressure stays constant (a free piston); a horizontal line (Figure 4.12); $W = P\,\Delta V$, and the heat raises the internal energy and does work. **Isochoric:** the volume stays constant (a rigid container); a vertical line (Figure 4.13); no work, so all the heat raises the internal energy.
b.

	Isothermal	Adiabatic	Isobaric	Isochoric
Constant	temperature	no heat flow ($Q = 0$)	pressure	volume
Equation	$PV =$ const	$PV^{\gamma} =$ const	$V/T =$ const	$P/T =$ const
P–V diagram	hyperbola	steeper curve	horizontal line	vertical line
Work	$nRT\ln(V_2/V_1)$	$nR(T_1 - T_2)/(\gamma - 1)$	$P\,\Delta V$	0
Heat	$Q = W$	0	$nC_P\,\Delta T$	$nC_V\,\Delta T$
ΔU	0	$-W$	$nC_V\,\Delta T$	Q
Speed, walls	slow, conducting	fast, or insulated	free piston	rigid container

17. a. An **adiabatic process** is one in which no heat is exchanged between the system and its surroundings ($dQ = 0$), because the system is insulated or the change is too fast for heat to flow.

Derivation, for n moles of ideal gas:

1. First law with $dQ = 0$: $nC_V\,dT + P\,dV = 0$.
2. From $PV = nRT$: $P\,dV + V\,dP = nR\,dT$, so $dT = \dfrac{P\,dV + V\,dP}{nR}$.
3. Substituting: $\dfrac{C_V}{R}(P\,dV + V\,dP) + P\,dV = 0$, so $(C_V + R)P\,dV + C_V V\,dP = 0$.
4. With $C_V + R = C_P$: $C_P P\,dV + C_V V\,dP = 0$. Dividing by $C_V PV$: $\gamma\dfrac{dV}{V} + \dfrac{dP}{P} = 0$.
5. Integrating: $\gamma \ln V + \ln P = \text{constant}$, so $\ln(PV^\gamma) = \text{constant}$, and $PV^\gamma = \text{constant}$.

b. $Q = 0$, so $\Delta U = Q - W = 0 - 1200 = \mathbf{-1200\ J}$: the internal energy falls by 1200 J.

c. $T_2 = T_1\left(\dfrac{V_1}{V_2}\right)^{\gamma-1} = 300 \times \left(\dfrac{1}{5}\right)^{0.4} = 300 \times 0.525 = \mathbf{157.6\ K}$.

$$W = \frac{nR(T_1 - T_2)}{\gamma - 1} = \frac{1 \times 8.314 \times (300 - 157.6)}{0.4} = \frac{8.314 \times 142.4}{0.4} = \mathbf{2.96 \times 10^3\ J}.$$

The textbook gives 118.8 K and 3768.3 J, but $300 \times 5^{-0.4}$ is 157.6 K, so those numbers don't work; the answers above follow from the question's data.

18. a. **Isothermal**, n moles at temperature T, from V_1 to V_2: $W = \int_{V_1}^{V_2} P\,dV$, with $P = nRT/V$ and T constant:

$$W = nRT\int_{V_1}^{V_2}\frac{dV}{V} = nRT\ln\frac{V_2}{V_1} = nRT\ln\frac{P_1}{P_2}$$

Adiabatic, from (P_1, V_1, T_1) to (P_2, V_2, T_2): $PV^\gamma = K$, so $P = K/V^\gamma$:

$$W = K\int_{V_1}^{V_2} V^{-\gamma}\,dV = \frac{K}{1-\gamma}\left(V_2^{1-\gamma} - V_1^{1-\gamma}\right) = \frac{P_1V_1 - P_2V_2}{\gamma - 1} = \frac{nR(T_1 - T_2)}{\gamma - 1}$$

using $KV_1^{1-\gamma} = P_1V_1$, $KV_2^{1-\gamma} = P_2V_2$ and $PV = nRT$.

b. $W = nRT\ln\dfrac{V_2}{V_1} = 1 \times 8.314 \times 300 \times \ln 4 = 2494.2 \times 1.386 = \mathbf{3457.6\ J}$.

19.

a. The **heat capacity ratio** γ (the adiabatic index) is the ratio of a gas's molar heat capacity at constant pressure to that at constant volume: $\gamma = C_P/C_V$ (equally c_P/c_V). It is always greater than 1.

b. By equipartition each degree of freedom holds $\frac{1}{2}RT$ per mole, so with f degrees of freedom $C_V = \frac{f}{2}R$, $C_P = \left(\frac{f}{2}+1\right)R$, and $\gamma = 1 + \frac{2}{f}$. Monatomic: 3 translational, $f = 3$, $\gamma = 5/3 = 1.67$. Diatomic: 3 translational + 2 rotational, $f = 5$, $\gamma = 7/5 = 1.40$. Non-linear polyatomic: 3 + 3, $f = 6$, $\gamma = 4/3 = 1.33$. The more atoms, the more degrees of freedom, and the smaller γ (and smaller still when vibrations join in at high temperatures).

c.

Reversible process	Irreversible process
Can be retraced so that the system and surroundings both return to their first states	Can't be retraced without leaving a change somewhere
Infinitely slow (quasi-static), in equilibrium at every step	Usually fast, through states not in equilibrium
No friction, viscosity or resistance; no energy dissipated	Energy is dissipated as waste heat
Total entropy stays constant	Total entropy increases
Can be drawn as a curve on a P–V diagram	Only its end states can be marked
An idealization (slow frictionless compression)	Every real process (rusting, friction, heat flowing from hot to cold)